Electronic supplementary information

Methanol-to-olefin conversion in ABC-6 zeolite cavities: unravelling the role of cavity shape and size from density functional theory calculations

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Table S1 Activity and selectivity of MTO conversion in different zeolites.

Catalyst	Topology	Cavity/ Channel	Life time (min)	Selectivity	Reference
SAPO-34	CHA	*cha*	550	> 80%	1, 2
SSZ-13	CHA	*cha*	600	40%	3
SSZ-39	AEI	*aei*	1200	50%	3
Sigma-1	DDR	*ddr*	250	not mentioned	4
SAPO-35	LEV	*lev*	100	not mentioned	5
DNL-6	RHO	*lta*	200	< 15%	6
ERI	ERI	*eri*	250	25%	7
SAPO-18	AEI	*aei*	300	< 50%	8
ZSM-11	MEL	3D channel	50	< 25%	9
ZSM-22	TON	1D channel	400	20%	10

Table S2 Calculated activation barriers (kcal/mol) for methylation reaction in different zeolites.

Method	Zeolite	Activation Barrier	Ref.
B3LYP/6-31G(d):PM6 // ωB97XD/6-311+G(2df,2p)	H-MCM-22	26.5 ~ 34.4	11
B3LYP/6-31G(d,p):PM6 // ωB97XD/6-311+G(2df,2p)	H-MCM-22	34 ~ 38	12
B3LYP/6-31G(d,p):PM6 // ωB97XD/6-311+G(2df,2p)	MFI	31 ~ 38	13
BEEF-vdW funcational	H-SAPO-34	17.8 ~ 30.4	14
GGA-PBE functional DNP basis set	H-SAPO-34	18.2 ~ 38.5	15
PAW-vdW funcational	MFI	34.6 ~ 49.5	16
ONIOM (ωB97XD/6-31G(d,p):mndo) // ωB97XD/6-31G(d,p)	MFI	22.1 ~ 35.5	17
ωB97XD/6-31G(d,p): MNDO)//ωB97XD/6-31+G(d,p)	ZSM-11 ZSM-22	25.0 ~ 49.6	18
PAW-vdW funcational	ZSM-11 ZSM-22	22.6 ~ 37.3	19
ONIOM(B3LYP/6-31+G(d):HF/6-31+G(d)) // ONIOM(B3LYP/6-31+G(d):MNDO)	CHA BEA MFI	19.4 ~ 46.5	20
ONIOM(B3LYP/6-31+(d,p):MNDO) // ωB97XD/6-31+G(d,p)	MFI DDR	33.5 ~ 46.1	21
OM(B3LYP/6-31+G(d):PM3 // ONIOM(M06-2X/6-31+G(d):PM3) // M06-2X/6-311+G(d)	H-SAPO-34	13.6 ~ 23.5	22
ONIOM(b3lyp/dgtzvp:MNDO) // ONIOM(b3lyp/dgtzvp:hf/dgtzvp)	SSZ-13	32 ~ 40.8	23
ONIOM(B3LYP/6-31+G(d):HF/6-31+G(d) // ONIOM(B3LYP/6-31+G(d):MNDO	MFI	23.7 ~ 52.3	24
Periodic and cluster models with various functionals	MFI	7.3~ 22. 5	25

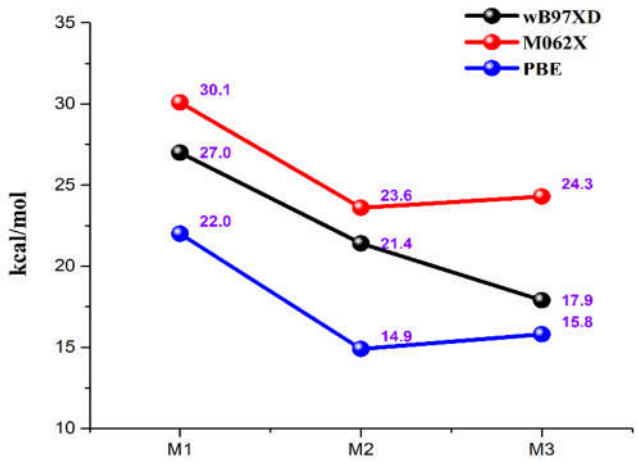


Fig. S1 Activation barriers for three methylation reactions in *cha* cavity by different functionals.

Table S3 Intermediates and transition states in *cha*, *avl, aft*, and *h1* cavities. E^{ele}: single-point electronic energy, G^{them}: thermal correction at 673 K. The unit is in Hartree.

Intermediate/ transition state	*cha*		*avl*		*aft*		*h1*	
	G^{them}	E^{ele}	G^{them}	E^{ele}	G^{them}	E^{ele}	G^{them}	E^{ele}
A	0.15200	-14930.29	0.146459	-17348.41	0.144509	-19766.5	0.153695	-19766.51
A + CH_3OH	0.18786	-15046.03	0.185988	-17464.15	0.182365	-19882.23	0.189024	-19882.25
TS-Me1	0.19278	-15045.99	0.187388	-17464.11	0.184884	-19882.2	0.195135	-19882.21
B + H_2O	0.19195	-15046.03	0.189178	-17464.15	0.182364	-19882.24	0.198333	-19882.25
TS-Dep1	0.20323	-15046.01	0.193359	-17464.12	0.188396	-19882.21	0.202762	-19882.21
C + H_2O	0.20001	-15046.01	0.193318	-17464.12	0.186359	-19882.21	0.202358	-19882.22
C + CH_3OH	0.21833	-15085.29	0.211175	-17503.41	0.207387	-19921.5	0.2192	-19921.5
TS-Me2	0.22362	-15085.26	0.216351	-17503.38	0.211278	-19921.47	0.228982	-19921.47
D + H_2O	0.21619	-15085.33	0.218343	-17503.46	0.211103	-19921.54	0.218726	-19921.55
D' + H_2O	0.21652	-15085.34	0.212427	-17503.46	0.210212	-19921.55	0.215909	-19921.56
TS-Elim1	0.20796	-15085.3	0.201741	-17503.42	0.199925	-19921.5	0.212638	-19921.51
A + C_2H_4	0.20415	-15085.31	0.196585	-17503.44	0.191202	-19921.52	0.211188	-19921.52
TS-Dep2	0.22321	-15085.3	0.215752	-17503.42	0.213503	-19921.51	0.227369	-19921.51
E + H_2O	0.21692	-15085.31	0.211923	-17503.43	0.206767	-19921.51	0.223288	-19921.52
E + CH_3OH	0.25093	-15124.59	0.233674	-17542.72	0.22824	-19960.8	0.240677	-19960.81
TS-Me3	0.24766	-15124.56	0.237669	-17542.68	0.233045	-19960.77	0.250106	-19960.78
F + H_2O	0.24287	-15124.64	0.23238	-17542.77	0.232711	-19960.84	0.250746	-19960.85
F' + H_2O	0.24028	-15124.64	0.230605	-17542.76	0.228233	-19960.85	0.244568	-19960.86
TS-Elim2	0.23796	-15124.61	0.226648	-17542.73	0.227132	-19960.82	0.242013	-19960.82
A + C_3H_6	0.23287	-15124.62	0.224509	-17542.75	0.210579	-19960.84	0.239715	-19960.83

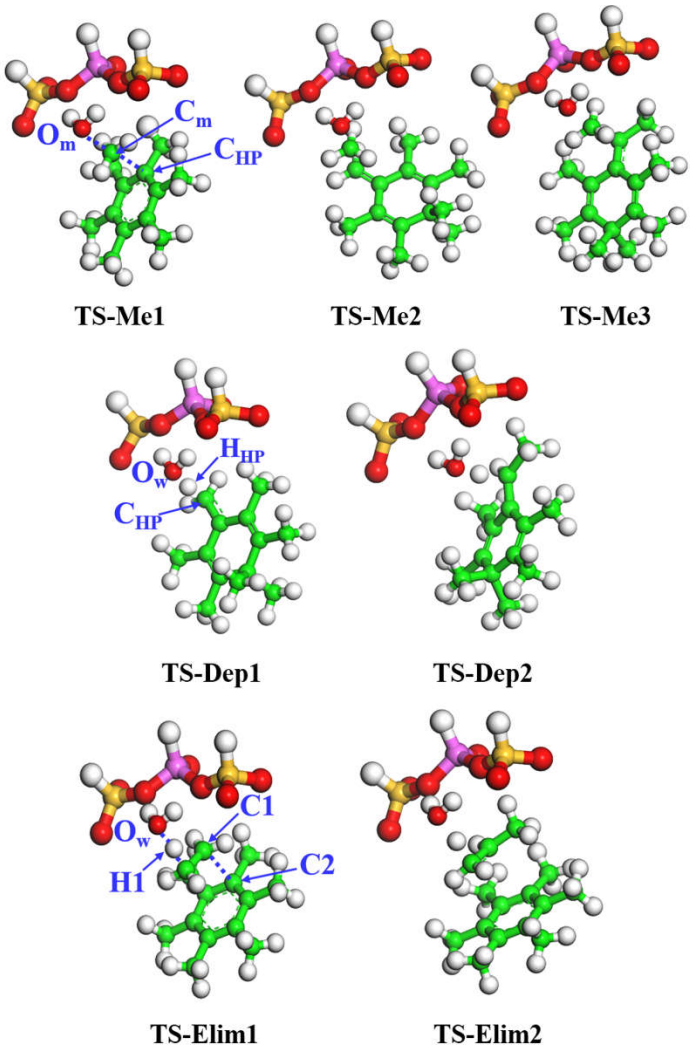


Fig. S2 Optimized transition states of methylations, deprotonations and eliminations in *cha* at the high level of ONIOM method. Si: yellow, Al: purple, O: red, C: green and H: white. O_m and C_m: O and C atoms in methanol. O_w: O atom in water. C1, C2, H1 and C_{HP}: C atoms in HP intermediates.

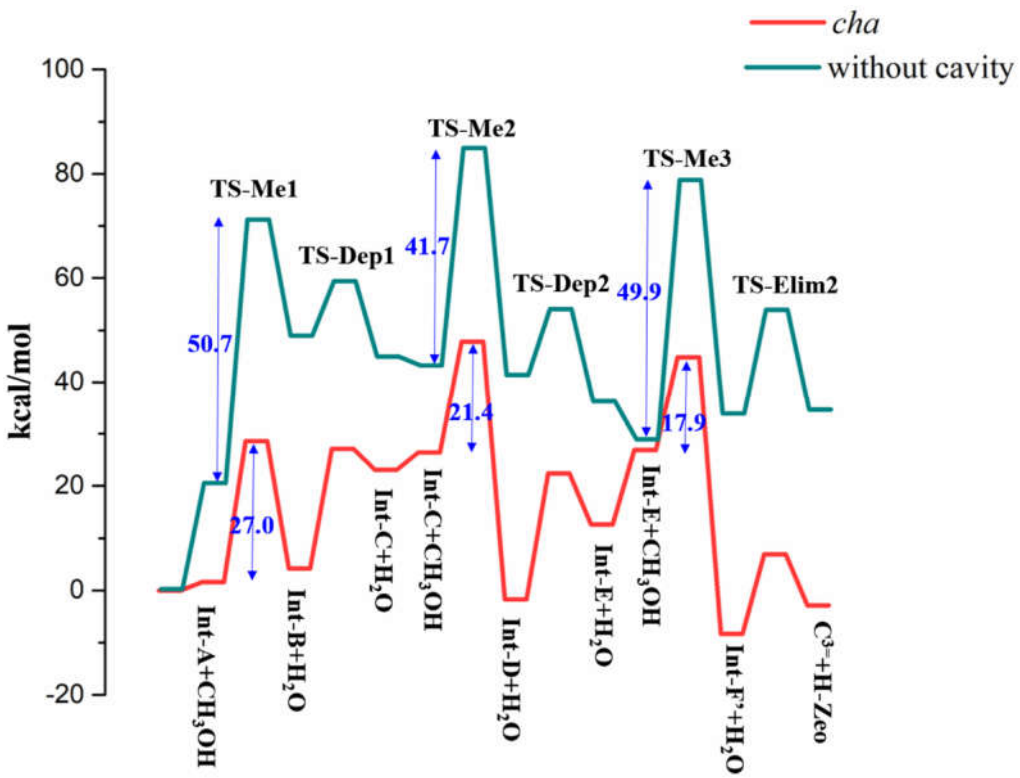


Fig. S3 Relative Gibbs energies of intermediates and transition states in *cha* and without cavity at 673 K.

Table S4 Bond distances (Å) in the transition states of methylations in different cavities.

Bond	*cha*			*avl*		
	TS-Me1	TS-Me2	TS-Me3	TS-Me1	TS-Me2	TS-Me3
C_m–O_m	2.14	1.99	2.00	2.15	1.99	1.99
C_m–C_{HP}	2.21	2.28	2.31	2.20	2.28	2.29

Bond	*aft*			*h1*		
	TS-Me1	TS-Me2	TS-Me3	TS-Me1	TS-Me2	TS-Me3
C_m–O_m	2.14	1.98	2.00	2.13	1.98	1.99
C_m–C_{HP}	2.19	2.25	2.28	2.20	2.27	2.28

O_m and C_m: O and C atoms in methanol. C_{HP}: C atoms in HP intermediates.

Table S5 Bond distances (Å) in the transition states of deprotonations in different cavities.

Bond	*cha*		*avl*	
	TS-Dep1	TS-Dep2	TS-Dep1	TS-Dep2
O_w–H_{HP}	1.23	1.27	1.23	1.23
H_{HP}–C_{HP}	1.41	1.38	1.40	1.41

Bond	*aft*		*h1*	
	TS-Dep1	TS-Dep2	TS-Dep1	TS-Dep2
O_w–H_{HP}	1.23	1.23	1.22	1.22
H_{HP}–C_{HP}	1.41	1.41	1.41	1.42

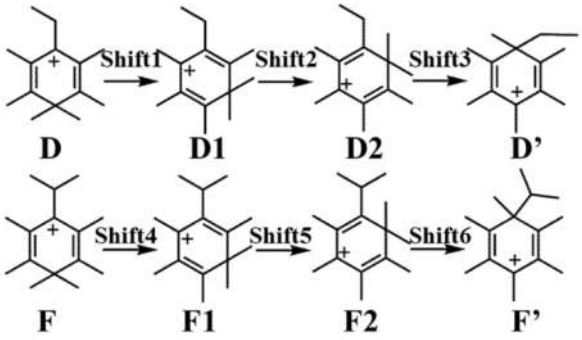
O_w: O atom in water. H_{HP} and C_{HP}: H and C atoms in HP intermediates.

Table S6 Bond distances (Å) in the transition states of eliminations in different cavities.

Bond	*cha*		*avl*	
	TS-Elim1	TS-Elim2	TS-Elim1	TS-Elim2
Ow–H1	1.48	1.50	1.48	1.55
H1–C1	1.24	1.24	1.25	1.22
C2–C_{HP}	2.71	3.07	2.73	3.07

Bond	*aft*		*h1*	
	TS-Elim1	TS-Elim2	TS-Elim1	TS-Elim2
Ow–H1	1.49	1.61	1.46	1.58
H1–C1	1.24	1.20	1.25	1.21
C2–C_{HP}	2.72	3.08	2.71	3.06

O_w: O atom in water. H1, H_{HP}, C1, C2 and C_{HP}: H and C atoms in HP intermediates.



Scheme S1 Methyl shifts during side-chain alkylation.

Table S7 Relative Gibbs energies (kcal/mol) of intermediates and transition states in different cavities.

Intermediate/ transition state	*cha*	*avl*	*aft*	*h1*
A + CH_3OH(g)	0.0	0.0	0.0	0.0
A + CH_3OH	1.6	3.5	3.2	0.6
TS-Me1	28.6	27.4	26.0	28.7
B + H_2O	4.2	3.9	-1.3	9.3
TS-Dep1	27.1	27.0	23.5	33.0
C + H_2O	23.1	24.8	20.7	29.3
C + CH_3OH	26.4	23.1	22.2	30.1
TS-Me2	47.8	45.5	41.3	56.2
D + H_2O	-1.7	-0.5	-4.7	2.8
D' + H_2O	-4.4	-4.0	-7.5	-7.6
TS-Elim1	15.3	14.6	12.8	19.2
A + C_2H_4	2.6	-0.7	-2.8	11.8
TS-Dep2	22.4	19.0	17.4	28.4
E + H_2O	12.6	14.6	10.7	21.2
E + CH_3OH	26.9	16.2	11.7	21.2
TS-Me3	44.8	38.2	33.6	47.2
F + H_2O	-9.5	-16.0	-9.7	-0.4
F' + H_2O	-8.3	-14.5	-17.9	-7.9
TS-Elim2	6.9	1.9	0.4	11.9
A + C_3H_6	-2.9	-12.9	-21.8	4.1

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